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FIFTH QUARTERLY REPORT

INVESTIGATION OF ELECTRODE MATERIALS FOR ALKALINE BATTERIES

JPL 952265

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ABSTRACT

The chronopotentiometric procedure for determining the diffusion coefficient of the silver species in concentrated KOH was found to be inapplicable. The capillary-diffusion method is now being used. The viscosities of KOH solutions ranging from 6 VF to saturated have been determined at 25°.

Preliminary experiments indicate that a thermal method for determining the silver species on an electrode is feasible. Wet samples can be dried near 100° without causing significant decomposition. AgO can be decomposed to Ag_2O at 230° without significant formation of metallic silver. Ag_2O can be reduced to the metal at 400°. The combination of decompositions should allow the determination of all silver species present.

Potassium-amalgam electrodes have been discharged at current-densities of about 8.1 A/cm^2 with about 80% recovery of charge. Similar electrodes have been charged at the same rate with 90% recovery of charge. There is evidence that the total amount of charge in the electrode affects the recovery, poorer recovery being obtained at higher total charge.

Initial gas-evolution experiments show that a potassium-amalgam electrode self-discharging into saturated KOH will lose about 2% of its initial charge in the first 5 days. The most rapid discharge occurs in the first few hours. Extrapolation of these data indicate that more than 125 days should be required for 50% self-discharge of this type of electrode.

The objectives of the contract are four-fold:

(1) Study of the reduction of Ag(I) by zinc.

(2) Study of the thermal decomposition of AgO and Ag_2O.

(3) Study of amalgam electrodes.

(4) Study of the evolution of gas at electrodes,

This report will be limited to the first three objectives.

A. DEPOSITION OF SILVER ON ZINC FROM KOH SOLUTIONS

It has been established that silver dissolved in concentrated KOH solutions is quite rapidly reduced by metallic zinc. The rate of self-discharge of a zinc electrode by this mechanism would be determined largely by the rate of diffusion of the silver species to the electrode surface. In order to estimate this rate, it is necessary to know the diffusion coefficient of the silver species at the KOH concentrations of interest.

Two methods seemed feasible for the diffusion determinations. Chronopotentiometry at various silver concentrations should permit the calculation of the diffusion coefficient from the variation of transition times.[1] The procedure would be rapid but depends on the validity of the Sand equation for the system. The capillary method of Anderson and Saddington[2] should also provide the information, but could be expected to be more tedious. Both methods were attempted.

Experimental

Transition times were determined with a Tektronix Model 564B storage oscilloscope using a Model 3A9 vertical amplifier and a Model 2B67 time base. External triggering was supplied from a 2-V lead-acid cell.

The cell container was a polyethylene bottle with the top cut off. The working electrode was a silver wire mounted in glass tubing with Epoxy

cement. The counter electrode was a platinum wire mounted in a glass compartment isolated from the test solution by a fritted glass disk. The reference electrode was a Hg/HgO electrode with a Luggin capillary mounted about 1 mm from the working electrode.

Constant current was supplied to the cell by an Electronics Measurements Model C629CMK power supply. In about half of the experiments the reference and working electrodes were connected directly to the input of the vertical amplifier of the oscilloscope to provide a direct measurement of electrode voltage vs time. In the rest of the experiments, the signal was put through a differentiating circuit made with a Heath Model EUW-19A operational amplifier module.

All chemicals were J. T. Baker Reagent Grade. KOH was obtained as 45% solutions.

KOH solutions of appropriate concentration were swept for 2 hours with nitrogen which has been passed through a vanadous chloride purifying train[3]. The solutions were allowed to stand undisturbed for about 10 minutes and then blank potentiograms were run at 50 μA. 1.00 ml of 1.85×10^{-2} VF $AgNO_3$ was added, the mixture was stirred with a Mag-Stir, and was allowed to stand for another 10 minutes. Potentiograms were again run a 50 μA. A similar procedure was used at other silver concentrations. Times were measured to the inflection points on the direct potentiograms or to the peaks of the derivative curves.

Viscosities of KOH solutions of various concentrations were measured in a water bath thermostatted at 25°±0.1° using Ostwald viscosimeters. Solution densities were determined with a pycnometer.

An Anderson-Saddington[2] type capillary diffusion cell was constructed from ordinary capillary tubing of about 1 mm I.D. These were cut into about 2-cm lengths, the ends ground flat and the bottoms sealed by cementing microscope cover glasses onto one end. The volumes were determined with mercury. The capillaries were mounted on a plastic disk which was attached to a glass support rod. The whole was mounted in a rubber stopper which served as the top of a polyethylene cell.

The main cell will contain solutions of various KOH concentrations and less than enough inactive silver to saturate the solutions. The capillary will contain a solution of the same concentrations of KOH and silver except that some of the silver present will be in the form of radioactive ^{110m}Ag. The whole system will be given sufficient time in the water bath to come to temperature equilibrium before the capillaries are lowered so that their open ends are below the surface of the cell solution. Diffusion will be allowed to take place over several days.

The radioactivity in the capillaries will be measured with a Model 703 Nuclear-Chicago liquid scintillation system as previously described.[4]

Results and Conclusions

The chronopotentiometric procedure for determining the diffusion coefficient did not prove feasible. Some typical derivative curves are shown in Figure 1. Figure 1a shows the blank trace, Figure 1b shows the trace for a solution which is 3.62×10^{-4} VF in Ag(I) and Figure 1c shows that for a solution which is 1.81×10^{-4} VF in Ag(I). The peaks are shown as minima because of the inverting property of the differentiator. The peaks represent inflection points in the chronopotentiograms; measurement of the times to the peaks allows determination of transition

times. Unfortunately, these curves are very complicated and interpretation has not been accomplished. The fact that some of the peaks seem to disappear altogether when the silver concentration is decreased makes the determination of a diffusion coefficient essentially impossible by the method. That the system is interesting from an electrochemical standpoint is obvious, but an investigation of its properties is not within the scope of this project.

It is necessary to know the viscosities of the solutions if any sense is to be made of the diffusion coefficients obtained. This information is not available in the literature for KOH solutions of the concentrations involved. The results of measurements made here are summarized in Figure 2. The values were determined with a relative precision of better than 0.5% at the 95% confidence level. One experiment was made with a solution saturated with Ag(I). Since the silver concentration was very low compared with the KOH concentration, it is not surprising that the silver had no measurable effect. No theoretical evaluation of the data has been made at this time.

Proposed Work

Experiments using the capillary diffusion method have just begun. These experiments will be continued until reasonable values of the diffusion coefficient have been determined at the appropriate KOH concentrations. Data will be evaluated and interpreted. This will conclude the work on this objective.

B. THERMAL DECOMPOSITION OF AgO AND Ag_2O

Earlier work has indicated that a thermal method of analyzing electrodes for all three species of silver might be feasible. By carefully controlling

oven and furnace temperatures, it should be possible to dry samples without decomposition and decompose AgO to Ag_2O without forming silver metal. While the procedure might be lengthy in terms of the time required for a single sample, many samples could be run simultaneously with little operator attention.

Experimental

Commercial AgO and Ag_2O was used without further purification. The AgO was obtained from Ames Chemical Works and the Ag_2O from K & K Laboratories.

Drying was accomplished in a Labline drying oven set at about 105°. The temperature varied about 3° each side of that value. Decomposition was carried out in a Tempco Model 1730B muffle furnace set at 230°. Temperatures varied as much as 10° about the nominal value. The true temperature may be different from the nominal since no attempt was made to calibrate the furnace pyrometer.

Sample sizes were about 0.3 g and were weighed and heated in glass weighing bottles.

Results and Discussion

In previous work with laboratory-prepared AgO, the materials have been dried in vacuum over P_2O_5 at room temperature in order to avoid any thermal decomposition. This drying process usually required several days and would impose a serious limitation on any method of analysis. No attempt had been made to determine how serious drying errors would be at 100°. Thus, the first problem was to determine whether moist AgO could be dried in the vicinity of 100° without significant decomposition. Samples of AgO were weighed and dried to constant weight. Several drops

of water were added and the samples again dried to constant weight. Changes in weight during this part of the procedure amounted to less than 0.3% relative, an insignificant amount for this analysis. It is evident that samples of the electrode material can be dried in an ordinary drying oven at about 100° without significant decomposition provided they are first washed free of alkali. No attempt was made to determine a maximum temperature for this part of the procedure because drying seems to be sufficiently rapid at the temperature employed.

Weighed samples of dry AgO and Ag_2O were placed in the muffle furnace. In the initial experiments, the temperature was set at a nominal value of 250°. The samples were generally heated for 4.5 to 5 hours the first time after which they were cooled and weighed. Heating was repeated until constant weight was obtained or until decomposition to the metal could be detected visually.

When the temperature was set at 250°, decomposition to metallic silver was obvious. Although, in general, the weight loss in the first heating period was close to the theoretically expected amount (6.46%), subsequent heating caused further loss--as high as 10.8% in these experiments. That, coupled with the appearance of silver particles, showed that decomposition of AgO and Ag_2O could not be carried out satisfactorily at this temperature. There was also visible indication of decomposition of commercial Ag_2O at this temperature. The product was not weighed.

The furnace temperature was lowered to a nominal 230° to see if this would slow the decomposition to silver metal. Preliminary results showed no significant decomposition of the commercial Ag_2O and about 1% less than the theoretically expected loss for the commercial AgO. The

first heating period was 4.5 hours and the second, 1.5 hours. There was no change in weight on the second heating indicating that 4.5 hours may be sufficient. However, in any practical analysis, a second heating would be made to ensure complete decomposition.

The apparently low amount of decomposition is not surprising because previous thermogravimetric measurements have indicated that the commercial AgO is not quite pure and probably contains some Ag_2O. At this point, no attempt has been made to complete the decomposition of the samples to the metal. Naturally, this step will be necessary for the complete analysis.

The preliminary work, as far as it has gone, indicates that this procedure is feasible as a method of analysis. It is apparent that the temperature control for the decomposition of AgO to Ag_2O is critical. If the temperature is just a little higher than the 230° used here, decomposition to silver will occur. If the temperature is much lower, the time required for the Ag(II) - Ag(I) transition is likely to be excessive. Temperature limitation will be investigated further.

Proposed Work

Work in progress will be continued. Samples will be decomposed to silver at about 400°, this being the optimum temperature indicated by thermogravimetric measurements. Experiments will be made using varying quantities of commercial AgO and Ag_2O in combination and both wet and dry. The results will be compared with those obtained by some of the classical methods.

Thermograms of AgO will be run in nitrogen and oxygen to see if they are affected by changing atmospheres. This work will begin as soon as equipment repair is completed.

C. AMALGAM ELECTRODES

Sodium- and potassium-amalgam electrodes reported previously[4] showed considerable promise of delivering energy at very high current-densities. Good behavior was observed at 1.2 A/cm^2. Shelf life seemed to be fairly satisfactory in some cases. Both of these aspects required further investigation since it was felt that the upper limits of current-density had not been reached and the self-discharge characteristics had been investigated only in a rather qualitative way.

Experimental

In order to obtain very high current-densities with the available equipment, it was decided to use hanging-drop electrodes. In this way, very small surface areas of reasonable accuracy could be obtained and small amounts of material would be required. The electrodes could be charged and discharged in the usual manner and the discharge behavior at high rates could be followed with an oscilloscope. At the highest rates, discharge times were less than one second.

Drop sizes were measured in solutions of each KOH concentration by collecting 10 drops in a cup from a Heath dropping-mercury-electrode capillary. The collected mercury was washed, dried, and weighed and the area of each drop calculated assuming them to be identical in size.

KOH solutions were prepared either from pellets or from 45% solution. The mercury was triply distilled.

The cell container was a 400 ml beaker with its top cut off and covered with a Teflon cover with holes drilled for the electrodes, capillary, etc. The hanging-drop working electrode was roughly centered in the cell. The auxiliary electrode was a platinum mesh cylinder about 4 cm in diameter.

The reference electrode was a Hg/HgO electrode with a Luggin capillary mounted as close as possible to the working electrode.

The power supply and measuring equipment have been described earlier in this report.

In the discharge-rate experiments, the working electrode was charged at about 27 mA/cm^2. The electrode was then discharged through the power supply at selected current-densities. In the charge-rate experiments, the charge rate was varied while the discharge rate was kept at about 135 mA/cm^2.

Measurements of self-discharge were made by measuring the rate of evolution of hydrogen with a Warburg manometer apparatus[5]. The mercury pool was contained in the center well of the Warburg flask. The diameter of the well was measured by pressing a slightly larger paraffin cylinder against the rim of the cup and then measuring the impression in the wax with calipers. The amounts of mercury and solution were kept as nearly as possible the same in each run.

To charge the electrode, an insulated platinum wire was passed into the mercury pool through the side-arm of the Warburg flask. The counter-electrode was a platinum wire dipping into the electrolyte solution. The amalgam was charged to 0.025 A-hr. Air was excluded during the charging period by passing nitrogen over the solution. The flasks were mounted in a Warburg water bath controlled at 26.2°; temperature equilibration was accomplished by leaving the flasks in the bath over night before charging was begun. After charging was complete, all stopcocks were closed and readings begun. The flasks were not agitated.

It has been assumed that the amalgams are charged with 100% current-efficiency. This is being checked by determining the potassium content

in some of the amalgams The procedure is the colorimetric method described by Kolthoff and Elving[6] with some modifications. There is a large amount of mercury in the presence of a small amount of potassium. The mercury will interfere with the analysis unless it is removed. The entire amalgam sample is first oxidized with nitric acid. The mercury is precipitated with hydrogren sulfide. The remaining potassium is then determined.

Results and Discussion

The effect of discharge rate on electrode capacity in saturated and 10 VF KOH solutions is shown in Tables 1 and 2. The electrode voltages were quite low during discharge at the very high current-densities. The voltage drops seem to be largely IR drops as indicated by the fact that the discharge curves are very flat until the end of the run. Thus, it seems that the electrodes themselves are behaving very well over the full range of current-densities.

Above a discharge rate of about 270 mA/cm^2, there seems to be a definite decrease in charge recovery until a rate of about 4.0 A/cm^2 is reached. Beyond this point, the recovery seem to be nearly independent of discharge rate, remaining around 80% for the saturated electrolyte system and a little less for the 10 VF system.

The initial amount of charge seems to have a definite effect on charge recovery in both saturated and 10 VF systems. In the saturated system, the recovery is 99% when the initial charge is about 4.5×10^{-5} A-hr while it is only 90% when the initial charge is 8.3×10^{-5} A-hr. Both of these discharges were made at about 2.7 A/cm^2. Similarly, the recovery at a similar current-density in the 10 VF system was 99% at

4.5×10^{-5} A-hr and 82% at 8.8×10^{-5} A-hr. The higher charge does bring the amalgam closer to saturation and it is possible that some gassing occurs during charge. However, this loss in capacity does not appear at 269 mA/cm^2 or less even at high total charge. Transport away from the electrode surface into the electrolyte solution is, no doubt, relatively slow compared to the rate of formation at the high discharge rates and it is possible that build-up of material on the surface makes the electrode process less efficient resulting in the lower recovery. When the total charge is less, discharge is complete before the build-up can occur. More work is necessary to investigate this phenomenon.

Charge rates seem to have less effect on the recovery than the discharge rates. This can be seen from the data in Tables 3 and 4. Recoveries of about 90% were obtained in both saturated and 10 VF systems at charge rates of about 8.1 A/cm^2. However, the amount of charge affects the recovery at high charge rates in much the same way it did at high discharge rates. This might be caused by a depletion of potassium ions near the electrode surface which sets up a diffusion-limited reaction after charging has progressed beyond a certain point. At lower current-densities or at shorter times, diffusion limitation may not occur. The mechanism must be different from that in the discharge case because the discharge rate is relatively low here.

The rate of self-discharge of the potassium-amalgam electrode into a saturated KOH solution is represented in Figures 3 and 4. The volume of gas evolved has been converted into microequivalents of potassium oxidized. The results have not been very consistent so far, but they do give an

indication of how much oxidation occurs over a given interval and how much might be expected over longer intervals. No attempt has been made to work out a rate expression. This will be deferred until more reliable data are available. However, it can be seen that about 2% of the original charge in the amalgam is discharged over a period of 5 days and that about a third of this discharge occurs in the first 24 hours. If discharge were to continue at the average rate of the first 5 days, one would expect 50% discharge in about 125 days. It is likely that the time would be much longer.

Proposed Work

Work on the charge and discharge rates will be continued using the sodium-amalgam system and, possibly, the lithium-amalgam system. Self-discharge will be studied further with the potassium-amalgam systems and various electrolyte concentrations as well as sodium-amalgam systems. Conventional stand-life experiments will be conducted to see how they compare with the gas-evolution experiments. Other solvent systems will be investigated.

Table 1

Effect of Discharge Rate on Electrode Capacity

Electrolyte solution is saturated KOH. Electrode A = 0.0327 cm^2 and is charged at 26 mA/cm^2. Precision of measurements is given at the 95% confidence level No precision is indicated if less than three measurements were made.

No. of Runs	Total Charge (A-hr x 105)	Discharge Current-Density (mA/cm^2)	Charge Recovery (%)
2	8.3	134	100
2	8.3	269	100
2	8.3	538	97.5
3	8.7	1344	91.7 ± 12.7
2	8.3	2688	90
3	4.5	2688	99.0 ± 2.5
2	9.0	4037	78.5
3	8.8	5376	77.3 ± 7.6
1	8.7	6720	74
3	8.4	7527	81.0 ± 4.3
8	8.6	8065	81.4 ± 2.6

Table 2

Effect of Discharge Rate on Electrode Capacity

Electrolyte solution is 10 VF KOH. Electrode A = 0.0368 cm^2 and is charged at 26 mA/cm^2. Precision of measurements is given at the 95% confidence level.

No. of Runs	Total Charge (A-hr x 10^5)	Discharge Current-Density (mA/cm^2)	Charge Recovery (%)
4	8.8	2717	87.8 ± 9.3
2	4.6	2717	99
4	8.9	4076	75.7 ± 2.4
6	8.6	5435	75.8 ± 8.2
8	8.1	6793	79.2 ± 4.4
4	8.3	7473	72.8 ± 17.0
12	7.6	8152	77.6 ± 3.9

Table 3

Effect of Charge Rate on Electrode Capacity

Electrolyte solution is saturated KOH. Electrode A = 0.0327 cm^2 and is discharged at 134 mA/cm^2. Precision of measurements is given at the 95% confidence level.

No. of Runs	Total Charge (A-hr x 10^5)	Charge Current-Density (mA/cm^2)	Charge Recovery (%)
5	3.6	2688	99.4 ± 1.1
3	1.5	5376	95.7 ± 9.4
4	1.3	6720	97.5 ± 4.0
9	1.3	8064	75.8 ± 3.5
9	0.78	8064	89.0 ± 4.3

Table 4

Effect of Charge Rate on Electrode Capacity

Electrolyte solution is 10 VF KOH. Electrode A = 0.0368 cm^2 and is discharged at 135 mA/cm^2.

No. of Runs	Total Charge (A-hr $\times 10^5$)	Charge Current-Density (mA/cm^2)	Charge Recovery (%)
2	4.6	2717	99
2	2.3	5435	94
2	1.3	8152	84
2	0.98	8152	96

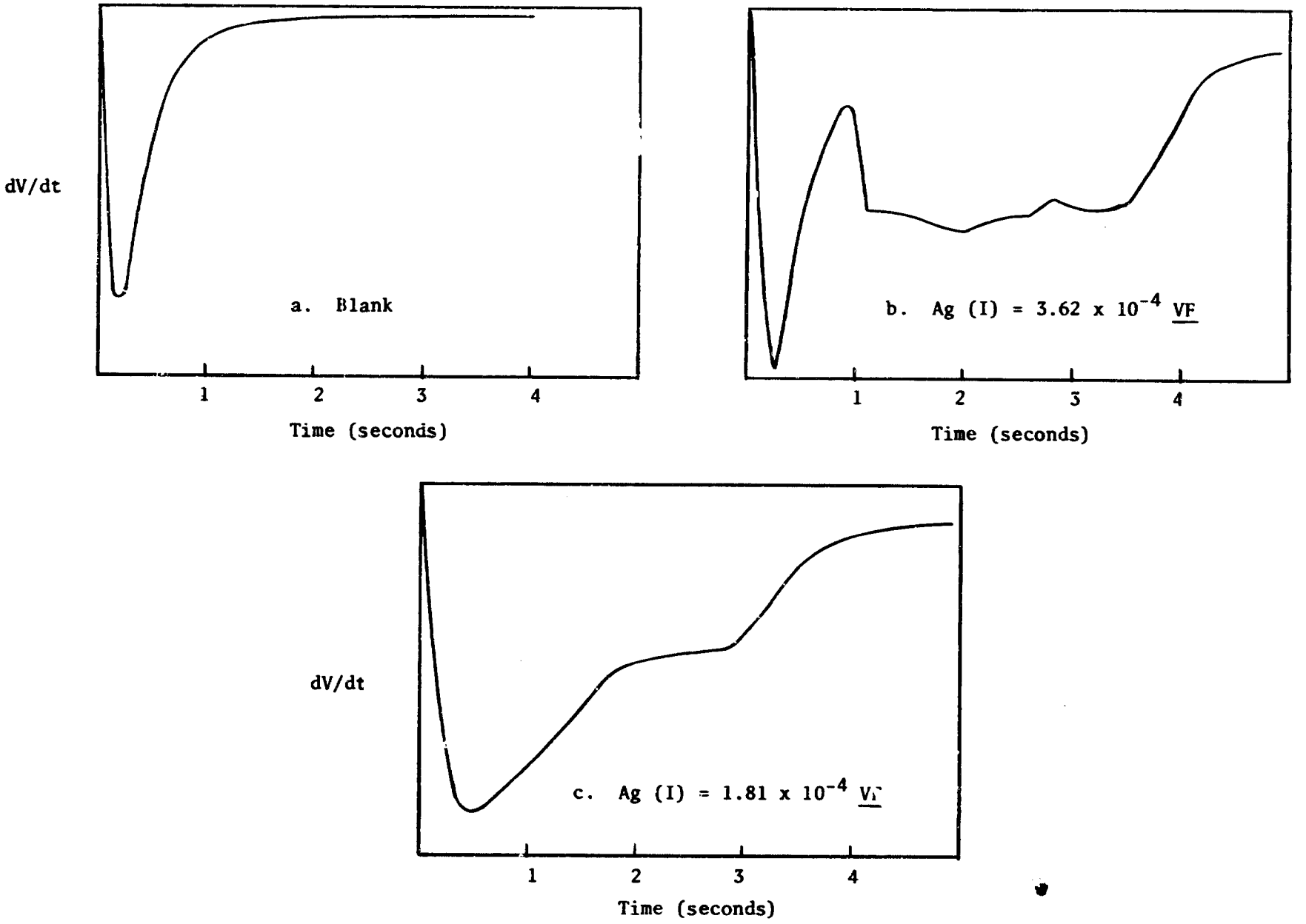

Figure 1. Chronopotentiograms of Ag (I) in 10 VF KOH

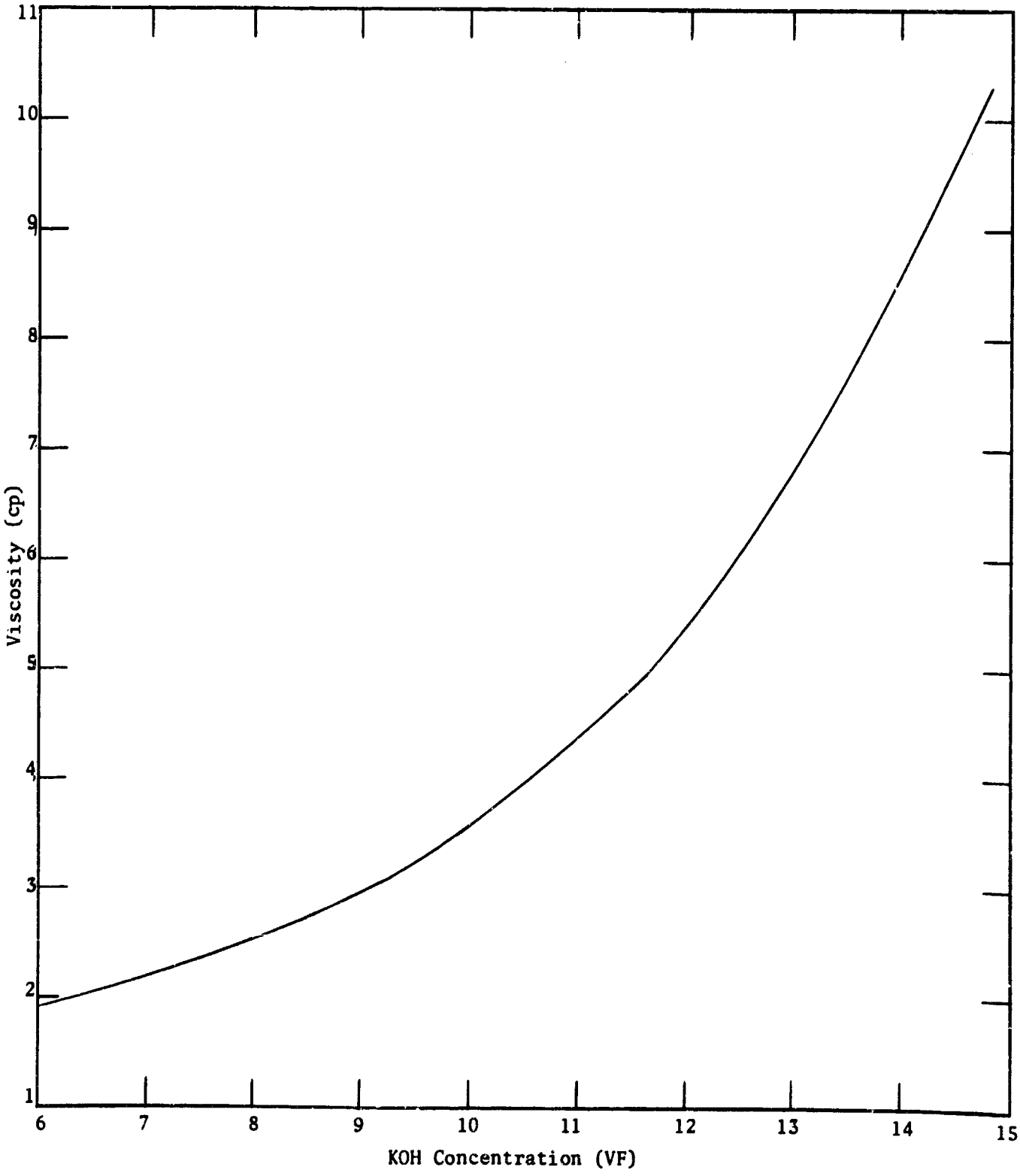

Figure 2. Viscosity of Concentrated KOH Solutions at 25°

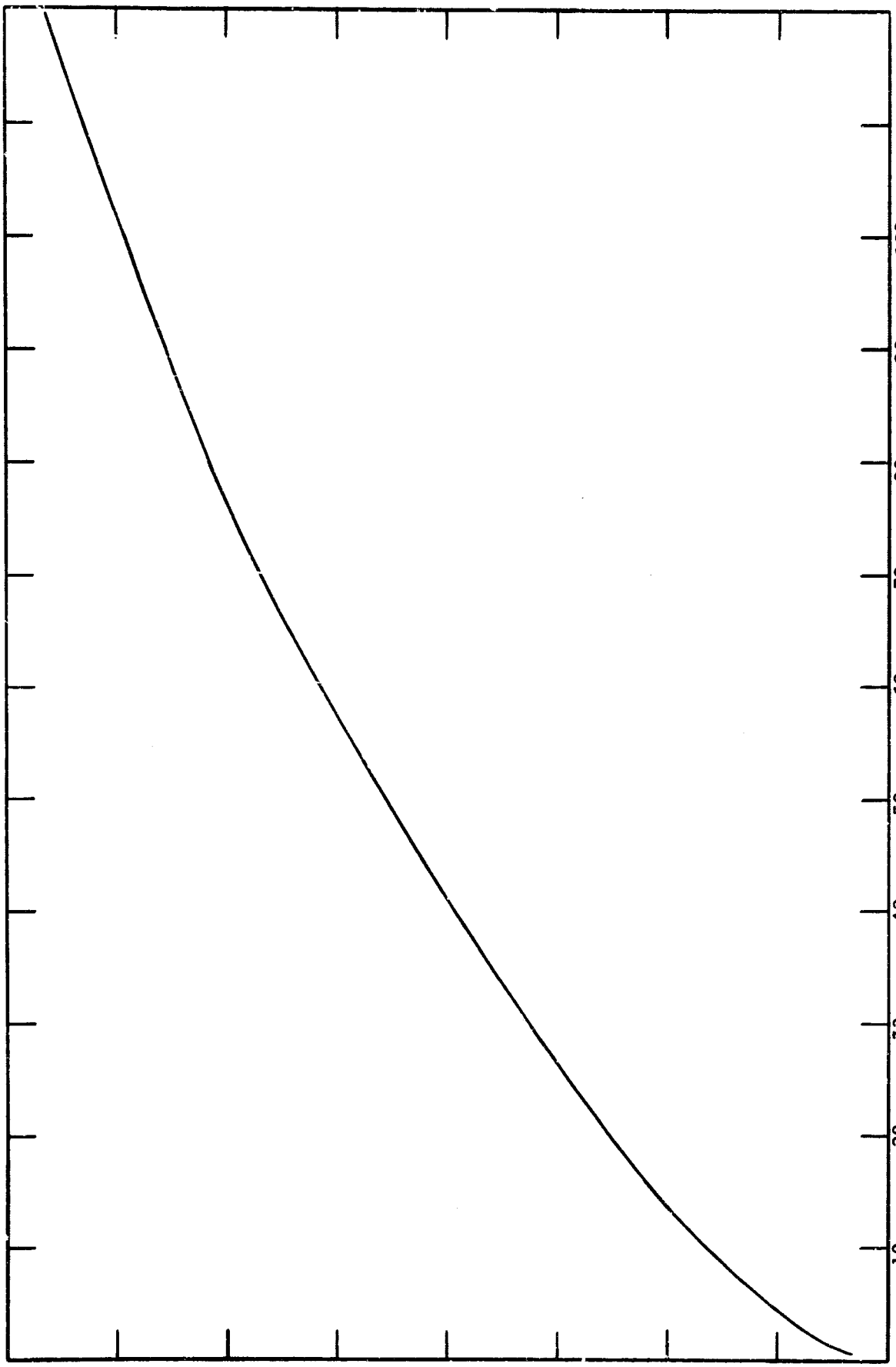

Figure 3. Rate of Self-Discharge of K(Hg) Electrode

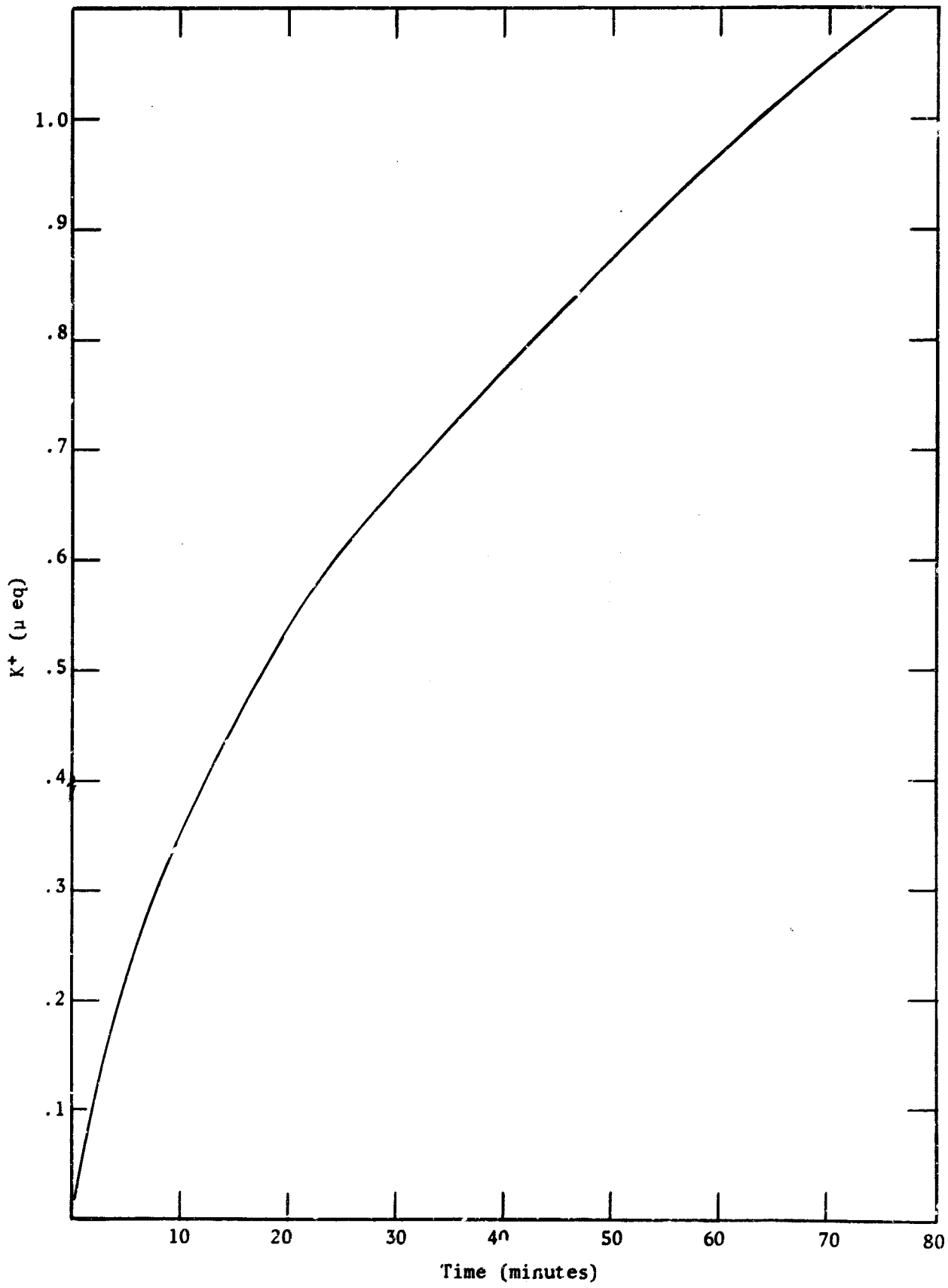

Figure 4. Rate of Self-Discharge of K(Hg) Electrode

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